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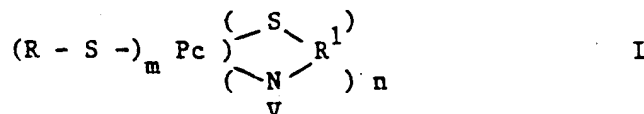
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(54) **Substituted phthalocyanine.**

(57) A phthalocyanine compound of the formula:



wherein

Pc is a phthalocyanine nucleus;

each R independently is optionally substituted phenyl;

m is 4 to 12;

V is H or C,  $\alpha$ -alkyl;

each R<sup>1</sup> independently is optionally substituted phenylene or naphthylene in which the S atom and group N-C are attached to adjacent nuclear carbon atoms;

and n is 2 to 6;

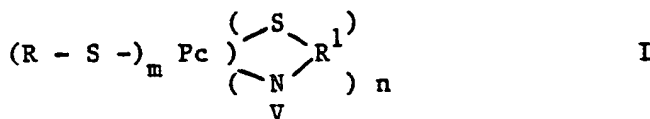
provided that R is not R<sup>1</sup>-NHV.

The compounds have a significant absorption band in the near infra red and are soluble in non-polar organic media. The compounds are useful in many applications where absorption of infra-red radiation is desirable, such as in OCR readable inks, security printing and reprographic toners.

# Substituted Phthalocyanine

This specification describes an invention relating to certain poly(substituted)phthalocyanine compounds which absorb in the near infra-red region of the electro-magnetic spectrum, e.g. at 700-1500 nanometres (nm) and specially at 750-1100 nm,

According to the present invention there is provided a phthalocyanine compound of the formula:



wherein

Pc is a phthalocyanine nucleus;

each R independently is a monovalent aromatic radical linked to a peripheral carbon atom of the Pc nucleus through S;

m is 4 to 12;

V is H or C,  $\alpha$ -alkyl;

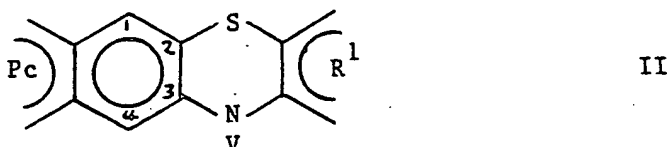
each R<sup>1</sup> independently is optionally substituted phenylene or naphthylene in which the S atom and group N-V are attached to adjacent nuclear carbon atoms in R<sup>1</sup>;

and n is 2 to 6;

provided that R is not R<sup>1</sup>-NHV.

The core of the phthalocyanine nucleus (Pc) may be metal-free or contain any of the metals or oxymetals which are capable of being complexed within the core. Examples of suitable metals and oxymetals are magnesium, palladium, gallanyl, vanadyl, germanium, indium and more especially copper, particularly copper(II), nickel, cobalt, iron, zinc, lead and cadmium. Where appropriate in this specification, a metal free phthalocyanine is designated, H<sub>2</sub>Pc and a metallised phthalocyanine such as copper(II) phthalocyanine is designated, Cu(II)Pc.

The S atom and the group N-V, are preferably attached to adjacent carbon atoms of the phthalocyanine nucleus, especially in the 4,5-positions, to form a 6 membered heterocycle fusing R<sup>1</sup> to the phthalocyanine nucleus, viz,

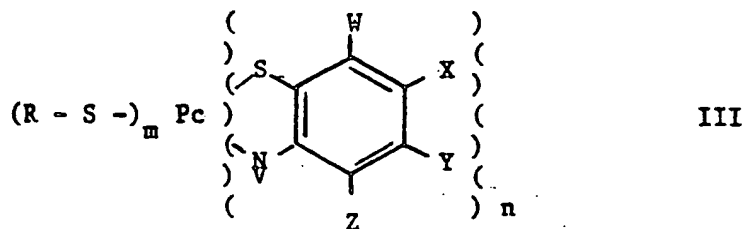


It is preferred that R is unsubstituted or substituted by from 1 to 3, more especially 1 or 2 groups, preferably situated in the ortho and or para positions with respect to the sulphur atom, selected from C,  $\alpha$ -alkyl, especially C,  $\alpha$ -alkyl, O-C,  $\alpha$ -alkoxy, especially O-C,  $\alpha$ -alkoxy, S-C,  $\alpha$ -alkyl, especially S-C,  $\alpha$ -alkyl, halogen, phenyl and acyl, such as COOH, COT<sup>1</sup>, CONT<sup>1</sup>T<sup>2</sup>, SO<sub>2</sub>T<sup>1</sup> and SO<sub>2</sub>NT<sup>1</sup>T<sup>2</sup> in which T<sup>1</sup> and T<sup>2</sup> are each independently selected from H, alkyl, especially C,  $\alpha$ -alkyl; aryl, especially phenyl and aralkyl, especially benzyl. It is also preferred that the average value of m is from 6 to 10 and more especially from 7 to 9. Where R carries two substituents these may be linked to form a second, fused ring, especially a benzene ring, when R represents a naphthyl group.

It is preferred that R<sup>1</sup> is phen-1,2-ylene or naphth-2,3-ylene or phen-1,2-ylene or naphth-2,3-ylene substituted by a group selected from any of the substituents listed above from R. Preferred substituents for R<sup>1</sup> are halogen and C,  $\alpha$ -alkyl. It is also preferred that the average value of n is from 3 to 5 and more especially 3.5 to 4.5.

It is preferred that 2n + m is from 13 to 16, and more preferably 14 or 15. The remaining substitutable positions on the phthalocyanine nucleus are preferably occupied by H, OH, C,  $\alpha$ -alkoxy, especially amyloxy and/or halogen atoms.

A preferred form of the compound of the present invention has the formula:



10 wherein Cu(II)Pc, R, V, m and n are as hereinbefore defined and W, X, Y & Z are each independently selected from H, halogen and C<sub>1-6</sub>-alkyl and more especially C<sub>1-4</sub>-alkyl, or any adjacent pair of W, X, Y & Z represents a fused benzene ring which may be free of substituents or substituted by any of the individual groups represented by W, X, Y and Z.

In an especially preferred compound of Formula II,

15 R is phenyl, 4-(C<sub>1-4</sub>-alkyl)phenyl or 4-(C<sub>1-4</sub>-alkoxy)phenyl;

m is 7 or 8;

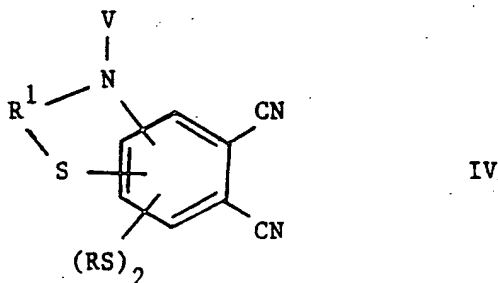
n is 4

V, W, X, Y & Z are H

and Pc is Cu(II)Pc.

20 The compounds of Formulae I and III may be prepared by reaction of a poly(halo)phthalocyanine, preferably one carrying from 13 to 16 halogen atoms, with a mixture of a thiol R-SH, and a thioamine HS-R<sup>1</sup>-NVH, in the desired molecular proportions, in the presence of an acid binding agent, such as an alkali metal hydroxide, e.g. KOH, at a temperature above 100°C, optionally in an organic medium. It is important to use a mixture of the thiol and aminothiols because introduction of the thiol prior to the aminothiols will lead to significant proportion of a phthalocyanine carrying only substituted-thio groups which is less bathochromic than the intra-molecular mixed product of Formula I or II.

25 Alternatively, the substituted phthalocyanine can be prepared from an appropriately substituted phthalonitrile of the formula:



35 or a mixture thereof with an unsubstituted phthalonitrile or a substituted phthalonitrile in which some of the substituents are replaced by hydrogen and/or halogen atoms. The phthalonitrile of Formula IV can be prepared by reacting a tetrahalophthalonitrile successively with one equivalent of the aminothiols, HS-R<sup>1</sup>-NVH, and two equivalents of the thiol, R-SH, under similar conditions to those employed from preparing the compound of Formula I from a poly(halo)-phthalocyanine.

40 The present compounds have a significant absorption band extending into the near infra-red region of the electromagnetic spectrum, i.e. from 700 to 1500 nm and thus have utility in applications where it is necessary or desirable to absorb infra-red radiation. Suitable applications are in solar and welding screens, in electronics, e.g. in wave guides, video disks, liquid crystal displays, etc. and in a wide range of laser-induced or laser-scanned systems, such as in inks for printing, optical character recognition (OCR) and security systems, e.g. in computer-controlled locks and alarms and for the formation of a security feature in currency, cheques, credit cards, etc.

45 The compounds of Formulae I and III have good solubility in non-polar organic liquids, especially those used in printing applications, such as ketones, e.g. methyl ethyl ketone (MEK), aromatics, e.g. toluene and chlorinated benzenes; aliphatic hydrocarbons, such as white spirit, petroleum fractions and chlorinated aliphatics such as dichloromethane. They are thus suitable for use in printing inks for the preparation of text which is to be read by optical character recognition (OCR) systems in the near infra-red.

The present invention is further illustrated by the following examples in which all parts and percentages

are by weight unless otherwise indicated.

### Example 1

2-Aminothiophenol (58.4g, 0.42 mol), 4-methylphenylthiol (99.2g, 0.08 mol), and potassium hydroxide (105.6g, 1.6 mol), were stirred in DMF (800 ml) at 120-130°C, for 40 minutes. To the mixture was added, portionwise over 30 minutes, commercial bromotetradecachlorophthalocyanine (VYNAMON Green 2GFW, 113.9g, 0.10 mol) and the mixture stirred at 125°C for 2 hours. After cooling to 80°C ethanol (1600 ml) was added to the stirred reaction mass in order to precipitate the product. The precipitate was filtered off and washed with ethanol and water. The paste was suspended in water, stirred, filtered, and washed with water and ethanol. The wet solid was dried in a vacuum oven at 40°C and 20 mbar.

Yield: 86g (42% theory)

WL<sub>max</sub>: 890nm (in CHCl<sub>3</sub>)

EC<sub>max</sub>: 46,000 (in CHCl<sub>3</sub>)

Solubility: >10% (in MEK)

WL<sub>max</sub> is the wavelength of the absorption maximum; and

EC<sub>max</sub> is the extinction coefficient at the absorption maximum.

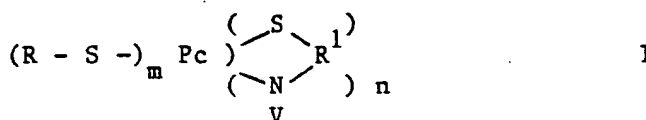
The product comprised a mixture of substituted-thio-CuPc with the average formula, hepta-(4-methyl-phenylthio)-tetra-(1-amino-2-thio-phen-1,2-ylene)-CuPc (HTCPC).

### Example 2

An 4% ink was prepared by dissolving HTCPC in MEK. The ink was applied to paper by gravure printing and the resulting print displayed very low reflectance (i.e. high absorption) in the range 750-900 nm and gave high print contrast ratios over this range. This demonstrates the suitability of the ink, and thus the compound HTCPC, for use in OCR.

### Claims

1. A phthalocyanine compound of the formula:



wherein

Pc is a phthalocyanine nucleus;

each R independently is optionally substituted phenyl;

m is 4 to 12;

V is H or C<sub>1</sub>;

each R<sup>1</sup> independently is optionally substituted phenylene or naphthylene in which the S atom and group N-V are attached to adjacent nuclear carbon atoms;

and n is 2 to 6;

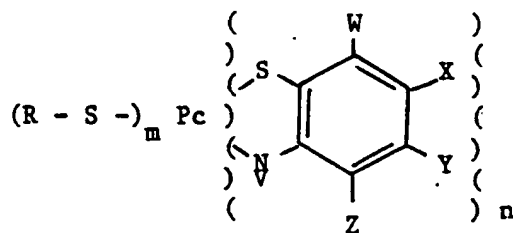
provided that R is not R<sup>1</sup>-NHV.

2. A compound according to Claim 1 wherein Pc is Cu(II)Pc.

3. A compound according to Claim 1 wherein R is phenyl, 4-(C<sub>1</sub>-alkyl)phenyl or 4-(C<sub>1</sub>-alkoxyphenyl).

4. A compound according to Claim 1 wherein m is 6 to 10, n is from 3 to 5 and 2m + n is from 13 to 16.

5. A compound of the formula:



10 wherein

RSP is a phthalocyanine nucleus;

each R independently is optionally substituted phenyl;

m is 4 to 12;

V is H or C<sub>1-6</sub>-alkyl;

15 each R<sup>1</sup> independently is optionally substituted phenylene or naphthylene in which the S atom and group N-V are attached to adjacent nuclear carbon atoms;

n is 2 to 6; and

W, X, Y & Z are each independently selected from H, halogen and C<sub>1-6</sub>-alkyl; or

20 any adjacent pair of W, X, Y & Z represents a fused benzene ring which is unsubstituted or substituted by halogen or C<sub>1-6</sub>-alkyl;

provided that R is not R<sup>1</sup>-NHV.

6. A compound according to Claim 5 wherein:

R is phenyl, 4-(C<sub>1-6</sub>-alkyl)phenyl or 4-(C<sub>1-6</sub>-alkoxy)phenyl;

m is 7 or 8;

25 n is 4

V, W, X, Y & Z are H

and Pc is Cu(II)Pc.

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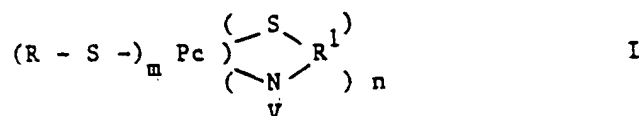
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EP 0 282 181 A3



EP 88 30 1306

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP-A-0 155 780 (IMPERIAL CHEMICAL INDUSTRIES PLC) * claims 1,7-10 * ---	1	C 09 B 47/04 C 09 B 47/20 C 09 B 47/18
A	GB-A-2 159 516 (CIBA-GEIGY AG) * claim 1 * ---	1	
A	EP-A-0 134 518 (YAMAMOTO KAGAKU GOSEI CO., LTD.) * claims 1-3 * ---	1,2	
A	DE-A-2 455 675 (CIBA-GEIGY AG) * claims 1-6 * ---	1,2	
A	GB-A-2 168 372 (SECRETARY OF STATE FOR DEFENSE) * claims 1-5 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 D 487/00 C 07 D 513/00 C 09 B 47/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 20-11-1989	Examiner HASS C V F
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	